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Benkoski, Jason J.

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The Johns Hopkins University Applied Physics Laboratory
11100 Johns Hopkins Rd
Laurel, MD 20723

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14. ABSTRACT

JHU/APL's Polymer Claw is a pressure-activated underwater adhesive that bonds instantly to biofouled surfaces in a single step. The key to this technology is the use of pressure sensitive microcapsules, which release reactive amine crosslinkers into an adhesive putty when pressed against the surface. The amine reacts with the sticky, isocyanate putty to form a tough polyurea. The catalyzed isocyanates likewise bond with alcohols, amines, acids, or oxides on the surface. This technology addresses the issue of biofouling through an abrasive metal brush coated with a caustic gel. Activated by water, the caustic removes plant and animal matter before the adhesive even makes contact with the surface. Pressure from the adhesive putty flattens the metal bristles and displaces the gel to make way for the adhesive. The entire system will be sealed in disposable packaging for safe storage and transport. This aggressive approach meets the Navy's requirements for speed, robust performance in all conditions, and no special training.

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POLYMER CLAW: INSTANT UNDERWATER ADHESIVE

Progress Report #8

Prepared for:

Dr. Reggie Beach
Office of Naval Research
Littoral Geosciences & Optics Program, Code 322
875 North Randolph Street, #1020
Arlington, VA 22203-1995

Prepared by:

Jason J. Benkoski, Ph.D., Senior Research Scientist
The Johns Hopkins University Applied Physics Laboratory
Research and Exploratory Development Department
11100 Johns Hopkins Rd, MS 21-N109
Laurel, MD 20723
Tel. (240) 228-5140

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1 Summary

When pressure was accompanied by a twisting motion, the caustic paste and abrasive brush successfully removed thick (> 2 mm) biofilms. Optimization of the pressure-activated adhesive is nearly complete. A 2:1 ratio of microcapsules:gorilla glue and a 1.5% dibutyltin diacetate concentration produced adhesion sufficient to break glass slides within 10 min. The second full Polymer Claw Prototype showed promise. The extra adhesive made full contact with the glass and largely displaced the caustic paste as it was pressed against the surface.

2 Project Goals and Objectives

For the next 2 months, we will continue the system-level development of Polymer Claw Prototypes. By the end of December, our final milestone is to adhere to a biofouled surface with an adhesive strength of 5 MPa under wet conditions.

3 Key Accomplishments

3.1 Biofilm Removal

To test the ability of the caustic paste and abrasive brush to remove biofilms, we prepared 20 aluminum panels with thick (> 2 mm) biofilms. The panels were immersed in the Chesapeake Bay from April to October. The biofilms included mostly algae with patches of barnacles.

3.1.1 Removal of Biofilm with Caustic Paste

The caustic paste was applied to the biofilms by spreading it across the surface with a metal spatula. The paste was allotted a fixed amount of time to digest the biofilm, and then the sample was rinsed gently with water. We observed intense outgassing (bubbling) and discoloration of the algae upon contact. Acting by itself, the caustic paste completely removed the biofilm within 10 min (Fig. 1). Although the CONOPS calls for removal of the biofilm within seconds, the caustic paste is not required to completely remove the biofilm by itself. It merely needs to weaken the film sufficiently for mechanical removal by the abrasive brush.

Figure 1: *Removal of biofilm by sulfuric acid paste.*

3.1.2 Combined Effect of Caustic Paste and Abrasive Brush

The next set of experiments evaluated the combined effects of the sulfuric acid paste and abrasive brush. For these experiments, the brush was coated with sulfuric acid paste and pressed against a biofilm-coated aluminum panel. The panel was then inspected afterwards to assess the amount of removed biofilm.

The first observation was that the number of bristles did not have a large impact on the amount of removed film. Lower bristle densities would therefore be preferred, because they do not require as much downward pressure. Figure 2 shows that the collapse of the bristles scraped away approximately 10% of the biofilm.

Figure 2: *Slide show of abrasive brush with 10 % bristles, 45° angle, and caustic paste.*

Figure 3: *Slide show of brush with 25 % bristles (50% on the sides); Caustic paste; underwater; 360° rotation:*

Much better results were observed when the brush was rotated 360° while it was pressed downwards. Figure 3 shows that the thick algae biofilm was completely removed under these circumstances. The combination of abrasive bristles, sulfuric acid, and rotation provided a clean surface for adhesive contact. We have already identified a built-in rotation mechanism that can rotate the abrasive brush without requiring the user to rotate the device manually. A design for the abrasive brush that automatically rotates when pressed down is detailed in the phase II proposal for this program.

3.2 Pressure-Activated Adhesive Optimization

Glycerol-loaded microcapsules with a tin catalyst cure the pressure-activated adhesive much more rapidly than amine-filled microcapsules. We hypothesize that the glycerol achieves better mixing, but we also believe that the catalyst may accelerate the reaction between the isocyanate adhesive and ambient moisture. Efforts this month have looked to optimize the concentration of catalyst and the ratio of microcapsules to adhesive.

The adhesive formulations were tested by clamping them between a pair of glass slides. After a fixed period of time, the slides were pried apart with a razor blade. If the glass slides failed, the time was noted. Here shorter times correspond to better performance. The adhesion results are listed in Table I below. The best performers generally had between 1% and 1.5% dibutyltin diacetate (DBTDA). They also had a 2:1 ratio (vol/wt) of microcapsules to gorilla glue. We note here that the volume of microcapsules is greatly underestimated due to the fact that they have a low density when they settle. Nevertheless, the microcapsules combine with the gorilla glue to form a viscous fluid that applies readily across glass slides. An example specimen is shown in Figure 4.

% DBTDA in microcapsules	Microcapsules : Gorilla Glue (volume : weight)	Time to break (minutes)
0.5%	1:1	20 (x2)
0.5%	1:2	>25
0.5%	2:1	20
1%	1:1	20 (x2)
1%	1:2	>30
1%	**2:1**	**15 (x2)**
1.5%	1:1	20 (x2)
1.5%	1:2	20 (x3)
1.5%	**2:1**	**10 (3 of 4)**
2%	1:1	>30
2%	1:2	20 (x2)
2%	2:1	20

Table I: *The curing time (time to break the glass slides) provided as a function of catalyst concentration and microcapsule loading.*

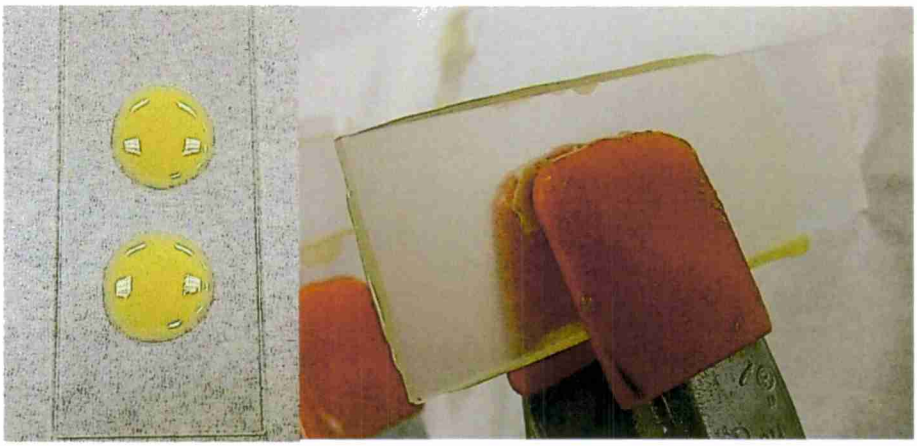

Figure 4: *Pressure-activated adhesive before and after clamping between a pair of glass slides.*

% DBTDA in microcapsules	Microcapsules : Gorilla Glue (volume : weight)	Time to break (minutes)
1.5%	2:1	10 (7 of 12)
1%	2:1	10 (11 of 12)

Table II: *The curing time (time to break the glass slides) provided as a function of catalyst concentration for the two best performing samples.*

To verify the optimum catalyst and microcapsule concentration, the two most promising candidates were repeated 12 times. For these trials, the 1% DBTDA samples performed slightly better. However, these samples also showed evidence of premature microcapsule rupture. This premature rupture was evidenced by the appearance of gas bubbles prior to clamping. These gas bubbles form when isocyanates react with water to produce carbon dioxide. The fact that outgassing occurred before clamping means that the catalyst was mixing with the gorilla glue before any pressure was applied. For this reason, the 1.5% DBTDA appears to be the best formulation moving forward.

3.3 Full Polymer Claw Prototype

The second full Polymer Claw prototype was fabricated with more adhesive and less caustic paste than the first prototype. To accommodate the additional adhesive, we lined the perimeter of the grill brush with high viscosity silicone grease. The prototype is shown in Figure 5. In these proportions, the volume of adhesive was sufficient to displace the majority of the caustic paste. The adhesive flowed past the bristles and made intimate contact with the surface. We also observed rapid outgassing once pressure was applied. The gas indicates that the gorilla glue was reacting with water to form a polyurea. The combination of water, DBTDA, and sulfuric acid appeared to accelerate the rate of cure relative to that seen in air. We were also pleased by the fact that the caustic paste did not appear to interfere with the spreading of the adhesive across the glass. One problematic issue, though, was the fact that the elastic springback of the metal bristles caused the prototype to detach once pressure was removed. This issue highlights the need for a design revision. The use of more compliant bristles or breakaway bristles will likely address this problem.

Figure 5: *Picture of full Polymer Claw prototype: sulfuric acid paste is tan, the adhesive is light yellow, silicone grease is translucent, and the plastic backing is dark gray. When pressed against glass while underwater, the adhesive displaces the caustic paste and spreads against the surface.*

4 Next Steps

4.1 Cold Water Measurements

Next month we will repeat the lap-shear experiments that were performed on samples that were prepared underwater. For this round, the samples will be prepared in ice water. The ice water will simulate the low temperature conditions under which this system will be expected to perform operationally.

4.2 Abrasive Brush Rotation

Given the success from rotating the abrasive brush on biofouled surfaces, we will investigate practical mechanisms for achieving this motion without creating additional burden or training for the user.

4.3 Prototype Testing

The next full prototype will be tested with a lower number of bristles that will be fatigued to the point of failure prior to use. By bending the bristles repeatedly, they will become embrittled to the point that additional plastic deformation will cause them to break off. Once broken, they will be unable to push the prototype off of the surface.